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13. ABSTRACT (Maximum 200 words)

This program evaluated a new technology for producing infrared photo-diodes in HgCdTe and InSb using evaporated organic heterojunctions. High quantum-efficiency IR detectors were demonstratedwith the organic process comparable to commercial IR detectors. The organic photo-diodes at room temperature were better than commercial detectors. They had lower leakage currents and higher resistance-area products (RoAs). Detector arrays made with the organics can operate at higher temperatures than the current detectors. Initial data at low temperatures were poorer than commercial detectors with lower RoAs and slightly higher 1/f noise. This comparison at low temperature may change with further optimization of the organic process. The organic diode process is very simple, low cost and non-damaging to the HgCdTe or InSb. It involves thermal evaporation of the organic onto the HgCdTe or InSb followed by evaporation of metal contacts through a shadow mask. Phase 1 demonstrated organic/HgCdTe IR detectors with quantum efficiencies similar to commercial devices operating at higher temperatures. The technology is ready for a Phase 2 to further optimize the processing for IR arrays and to increase yields.

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ORGANIC/ IR-SEMICONDUCTOR HETEROJUNCTIONS FOR LOW-COST, HIGH TEMPERATURE IR ARRAYS

FINAL REPORT

AUGUST 30, 1992

BY

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EXTENDED ABSTRACT

This Phase 1 program evaluated a new technology for producing infrared photo-diodes using evaporated organic semiconductor heterojunctions. The technology is important because it is a benign, simple process with the potential for higher-temperature operation and lower costs than is available using standard IR detectors.

The program succeeded in demonstrating organic/HgCdTe IR detectors with quantum efficiencies comparable to commercial detectors and with lower leakage and higher resistance data at high temperatures than commercial detectors.

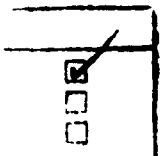
Before this program, organic/ HgCdTe and /InSb diodes had been made with very low room-temperature leakage currents, very high resistance-area products (RoAs) and very high reverse-bias breakdown voltages. There was no optical data. The major question was whether the good high-temperature data was due to junction barriers that lowered leakage currents but would also reduce photo-detection. This program determined that the very low-leakage, high-temperature diodes did have junction barriers and low quantum efficiencies. However, organic diodes were demonstrated without the barriers with high quantum efficiencies and better high-temperature characteristics than standard implanted or double-layer IR diodes.

The current organic/ HgCdTe diodes have poorer leakage, RoA and 1/f noise characteristics at low temperatures than the standard diodes. This data compares data from some of the first organic/ HgCdTe diodes with the better commercial detectors with over fifteen years of process development. Further development of the organic process may improve the low temperature comparison. Specifically the low temperature organic data seems to be limited by tunneling. If this can be reduced, the low-temperature leakage and 1/f noise will also be reduced.

The organic process is very simple and low cost involving the thermal evaporation of the organic onto the HgCdTe or InSb followed by the evaporation of a metal contact through a shadow mask. The HgCdTe stays at room temperature or lower for the junction formation process and the organic contacts the HgCdTe with weak van der Waals forces that do not damage the base material. This is especially important for HgCdTe and InSb which are very fragile and show thermal decomposition and defect formation at relatively low processing temperatures.

The process for these small bandgap semiconductors currently has low yield and uniformity. The process is adequate for test devices or small linear array production but new procedures are needed for a large array technology.

Good high quantum efficiency IR detectors have been demonstrated with the organic process that operate at higher temperatures than standard IR diodes. A Phase 2 program is needed to further optimize the process, improve yields and test large array processing.



BACKGROUND

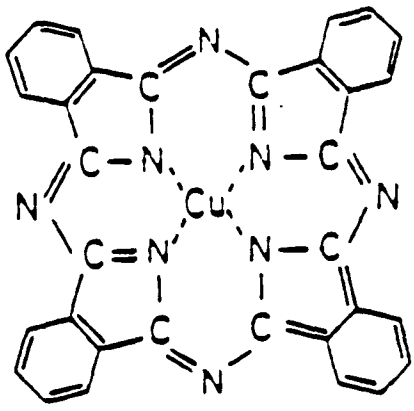
There has been extensive study in the last fifteen years in the field of organic semiconductors (1). Many of these organics show n and p-type conductivity. Mobilities, resistivities, carrier concentrations, doping and trapping effects have been characterized.

A subset of these compounds has been developed that form useful barrier junctions with inorganic semiconductors (2,3). These junctions show very low leakage currents and very high reverse bias breakdown voltages. Information on some of these is given in Table 1 (2). The table shows that organic heterojunction diodes have been formed on both n- and p-type Si, Ge, GaAs, InP, CdTe, HgCdTe and InSb (3,4). The major application for HgCdTe and InSb is in infrared detectors operated at low temperatures. While electrical diode data was taken, no optical data had been measured. This program was set up to determine the usefulness of the organic diode technology for producing IR detectors. Of special interest was to determine the quantum efficiency, high temperature operation, noise and process yield.

The organics studied in this program all have large planar structures. The structures for 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) and copper phthalocyanine (CuPc) used in this program are diagramed in Figure 1. These organics have low vapor pressures (they are high vacuum compatible). They are stable to high temperatures, withstanding vacuum-bakeout at 120 C for several weeks (5) and evaporating without structural breakdown at temperatures of 450 to 600 C depending on the compound. The evaporated material forms a crystalline structure on a target substrate with weak van der Waals forces between the organic molecules and between the organic and the inorganic substrate. These forces are so weak that the rearrangement to crystalline form can take place even at liquid nitrogen temperatures (2,6).

The highest filled and next unfilled energy bands correspond to p orbitals perpendicular to the plane of the organic molecule. The electrical conduction in these crystals is large in the direction perpendicular to the plane of the molecule along the direction of the p orbitals and the conductivity is very small in the molecular plane. An organic/inorganic diode is made by evaporating the organic onto the semiconductor and then a shadow mask is used to define metal contact areas. The directional conductivity of the organic means that the current flows down from the metal into the semiconductor and not between contacts. A device is shown in Figure 2 and a suggested band diagram for the junction is shown in Figure 3. The fact that the current flows into the semiconductor perpendicular to the surface minimizes surface effects like pinch off fields that increase tunneling and leakage currents. Data for silicon-organic diodes are shown in Figure 4 showing the low leakage current and the high reverse bias breakdown voltage (7).

CuPc



PTCDA

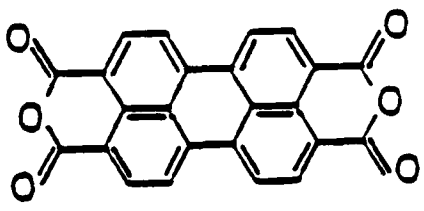


Figure #1 Molecular structure of CuPc used with HgCdTe and PTCDA used with InSb to form organic/ inorganic semi-conductor diodes.

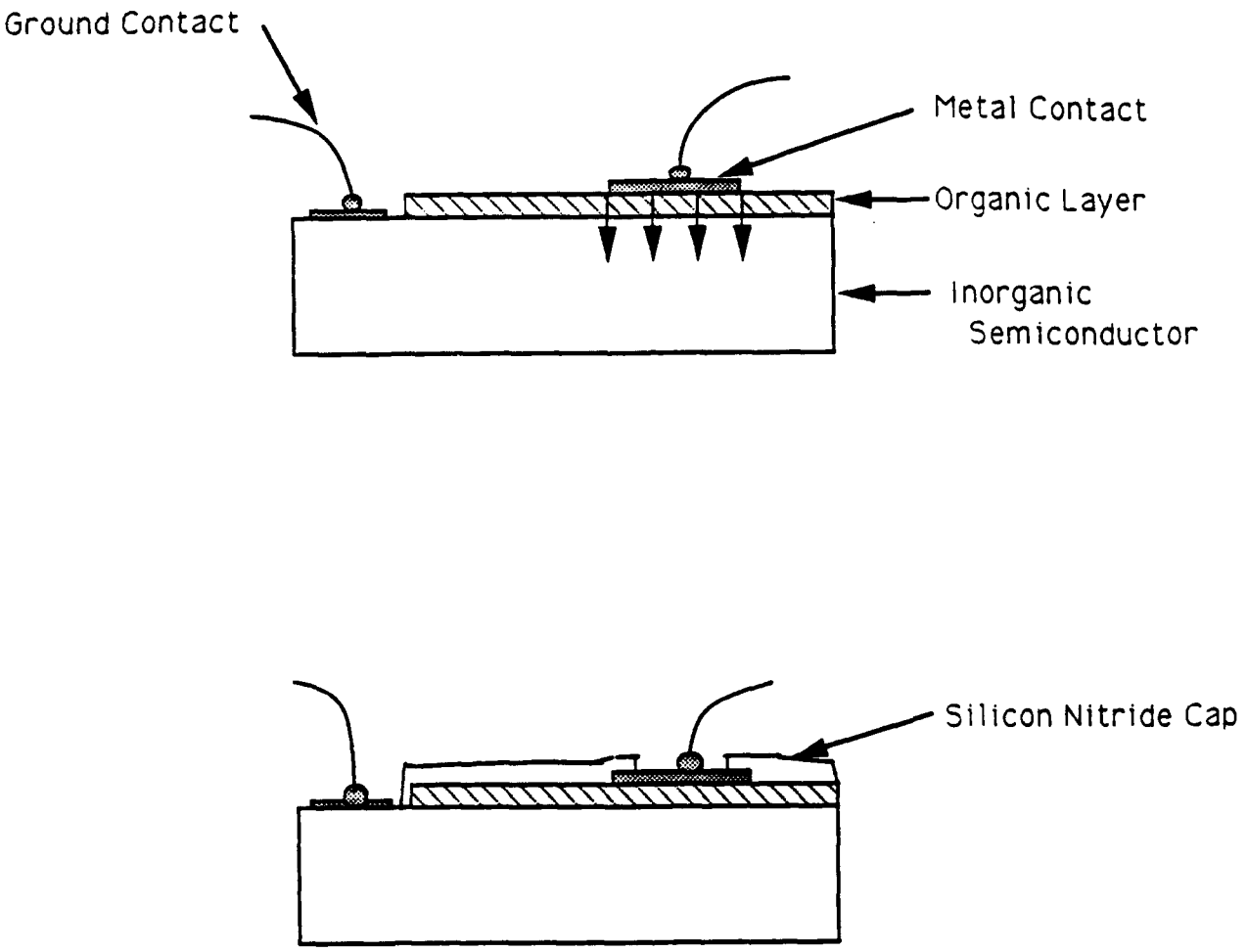


Figure #2 Diagram of the organic / inorganic semiconductor diode formed by an evaporated organic layer and a metal contact evaporated through a shadow mask. A silicon nitride cap is shown in the lower structure. The current is fixed by the organic's one directional conductivity to flow approximately perpendicularly to the surface.

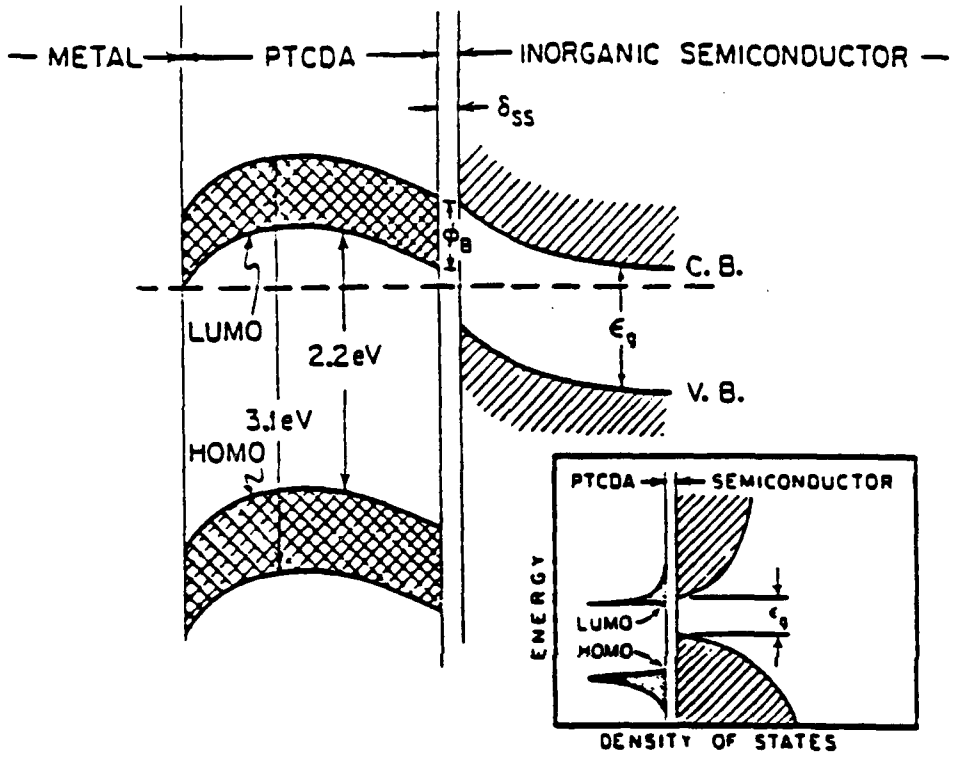


Figure #3 Band diagram of an organic on n-type inorganic semiconductor junction. LUMO is the lowest unfilled molecular orbital and HOMO is the highest occupied molecular orbital in the organic. The gap between the PTCDA and the inorganic is to represent the possible presence of an insulating surface layer.

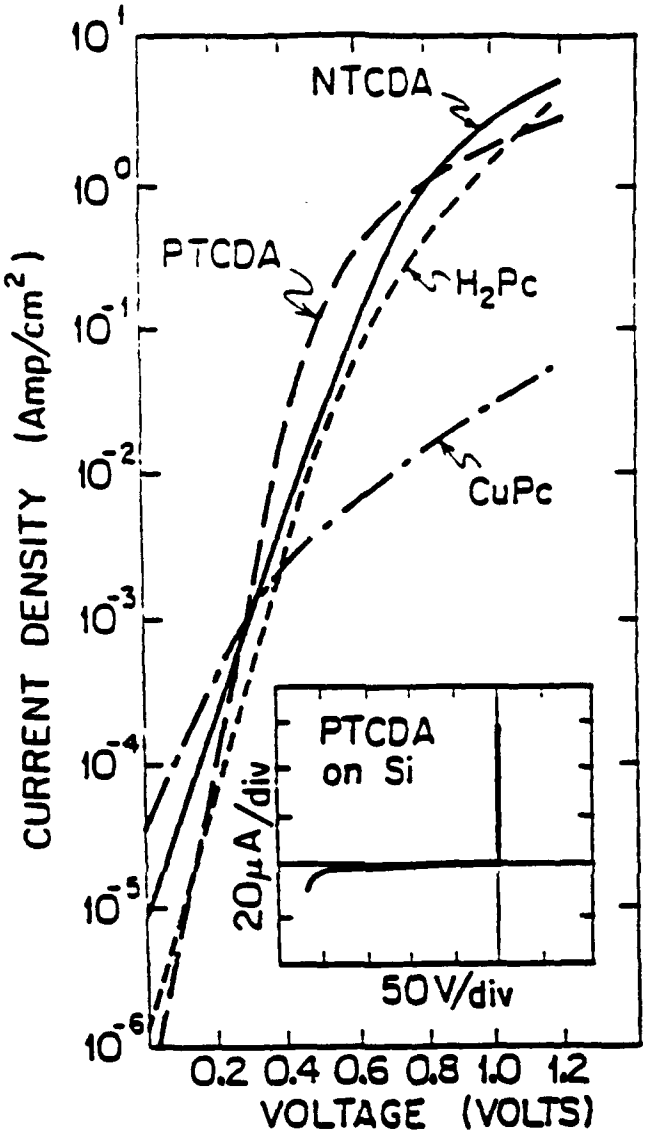


Figure #4 Forward bias current verses voltage for various organics on p-type silicon at room temperature. The inset shows the low leakage and high reverse breakdown voltage.

The original organic studies were with large band-gap semiconductors so it was an important result to find that the low leakage, high breakdown voltage and high temperature operation held for HgCdTe(4) and InSb (2).

Data are shown for these materials in Figures 5 and 6. The problem was that the data was too good. It was not known whether the good low leakage results were due to surface insulating barriers that lowered the leakage but would also limit the photodetector collection (quantum efficiency). No optical detector data had been taken.

If the quantum efficiencies are high, there are several potential advantages to these organic/inorganic semiconductor diodes for use in producing infrared detectors. These include:

- Benign Junction Formation
  - No strain, no misfit-dislocations, no cap-layer interdiffusion
  - No high-temperature processing for cap-layer growth, implant annealing or diffusion
  - No interface damage and no degradation of the starting material,
- Simple Process
  - Evaporated organic and metal contact
  - Potential low-cost process
- Low-leakage Diodes
  - Potential photo-detectors
  - Higher temperature detector operation.

PROGRAM OBJECTIVES

The objective of the Phase I program was to characterize the optical and electrical properties of the organic on HgCdTe and InSb diodes to determine this technology's importance in infrared detector applications.

Specific objectives were to:

- Evaluate two organic materials with good junction properties on HgCdTe,
- Charactize the optical detector properties and
- Evaluate the DoD and commercial potential of these devices.

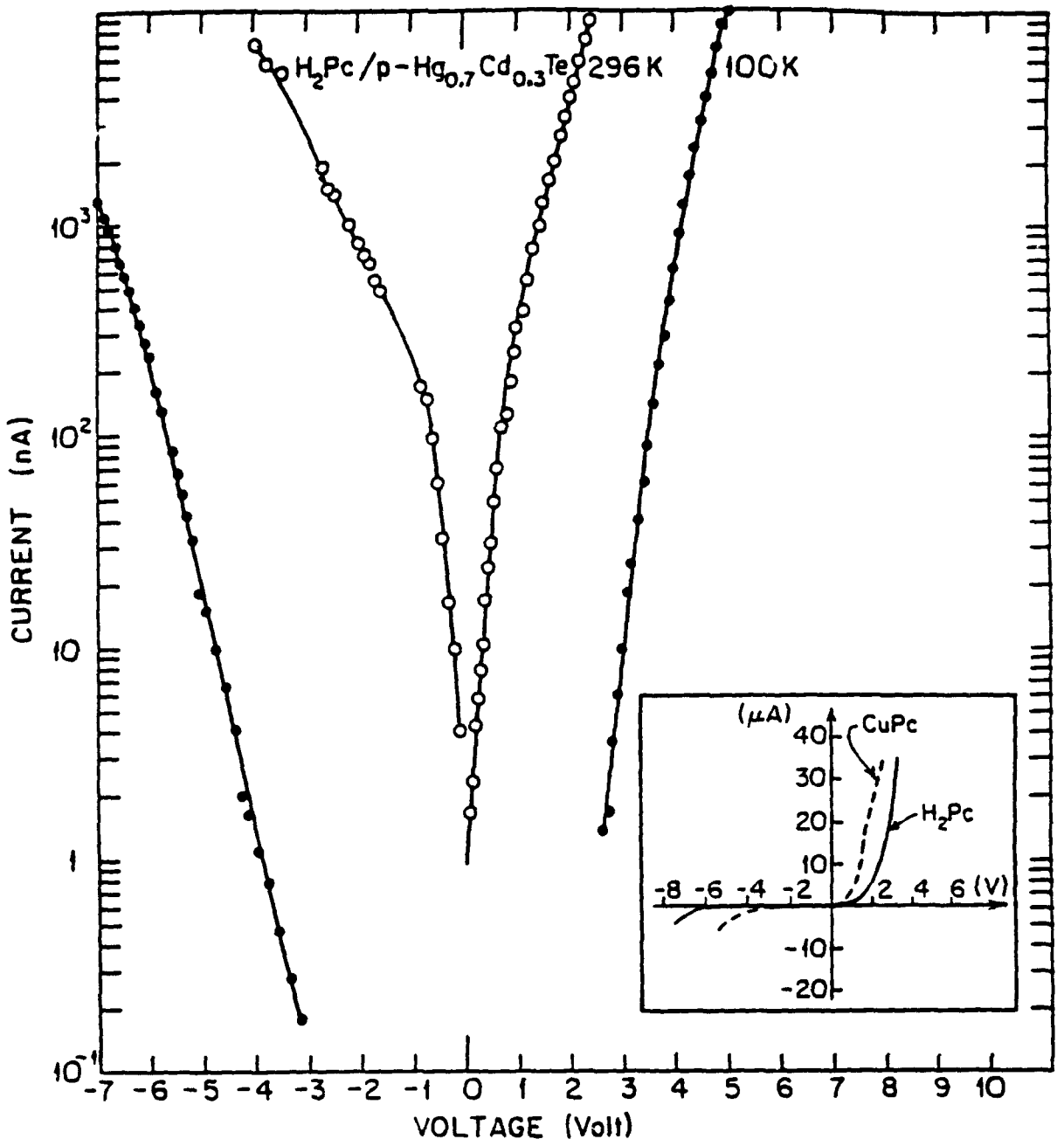


Figure #5 Current-voltage data for x=0.3 HgCdTe at 100K and 296K with the inset showing the low leakage and high breakdown voltage at room temperature. The room temperature gap energy is 0.295 eV.

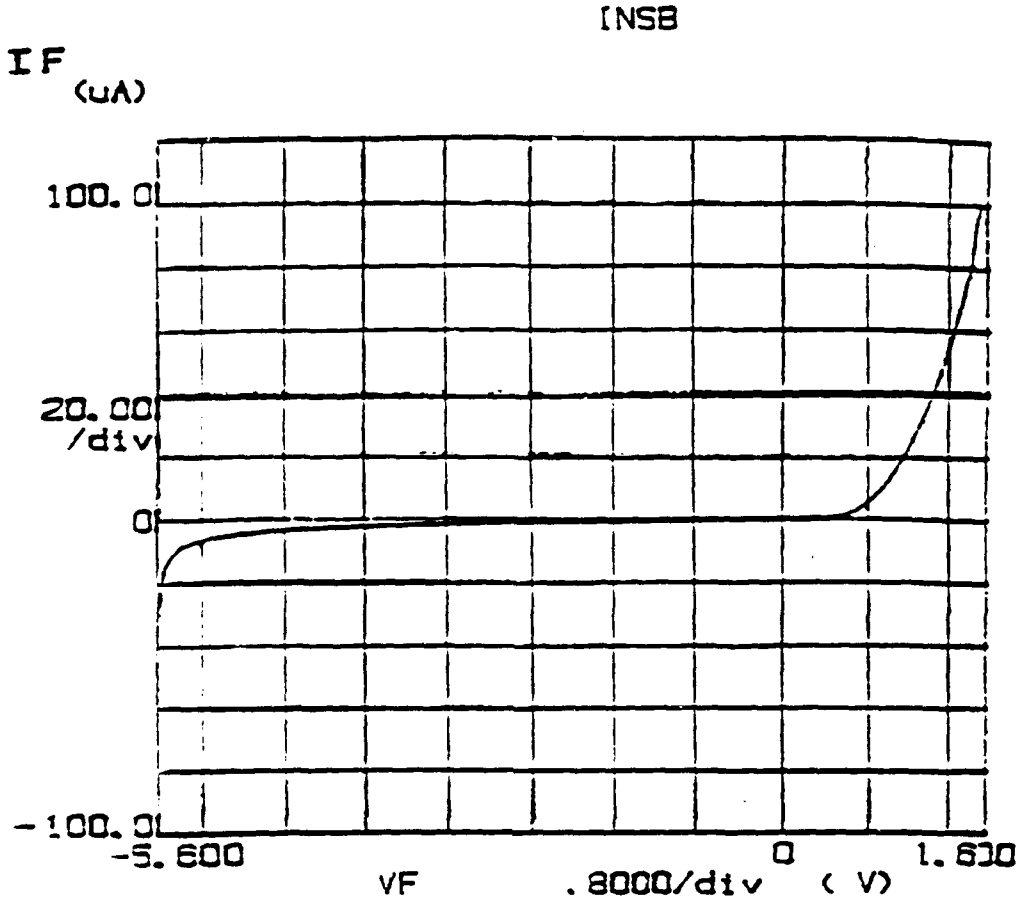


Figure #6 Room temperature current-voltage data for InSb. The room temperature gap energy is 0.17 eV.

EXPERIMENT

The organic chemicals used in this program are sold as dies and must be purified before use in semiconductor devices. This purification was carried out at the University of Southern California using the technique of vacuum sublimation. The setup is shown in Figure 7. The organic was heated in a quartz tube with a temperature gradient for three days to sublime the material in vacuum. Higher sublimation temperature impurities remained at the original sample position in the tube while lower temperature materials deposited in the cooler regions of the tube or were pumped out. The sublimed material was then heated in a cleaned tube to just under the sublimation temperature for three days again under vacuum to drive off residule solvents and low vapor pressure impurities. The purified material was stored in dry nitrogen.

A standard thermal evaporation chamber at Santa Barbara Focalplane was modified in several ways for depositing the organic layers. Two thermal sources were used, one for the organic and one for indium for metal contacts. The samples were held on a copper base plate of a liquid nitrogen reservoir. A slider was used to move a shadow mask over the sample after the organic deposition and before the indium deposition. The chamber is diagrammed in Figure 8. The deposition rate and the film thickness were monitored with a crystal monitor. The organic was deposited very slowly at 2 to 3Å per sec. CuPc was deposited to a thickness of 500Å onthe HgCdTe samples while PTCDA was deposited to a thickness 1000Å on the InSb samples. The indium contacts were deposited through a shadow mask at a rate of 8 to 15Å per second to thicknesses of 2000Å to 4000Å. The shadow mask pattern is shown in Figure 9 and has variable area and variable permitter devices along with a small 2X16 array. The sample temperatures during the depositions ranged from 87 to 93 K. For most depositions the sample was not exposed to air between the organic and the indium depositions.

The semiconductors used were mid-wavelength (x=0.25 to x=0.3) epitaxial HgCdTe from Fermionics and SBRC and bulk InSb from Johnson Matthey.

Electrical measurements were made either in a dry nitrogen probe station at room temperature and 77K or in an optical vacuum dewar with the samples mounted in an 84 pin flat pack with a hole in the bottom of the flat pack to allow a known flux of radiation from a black body to hit the sample backside. This is diagramed in Figure 10.

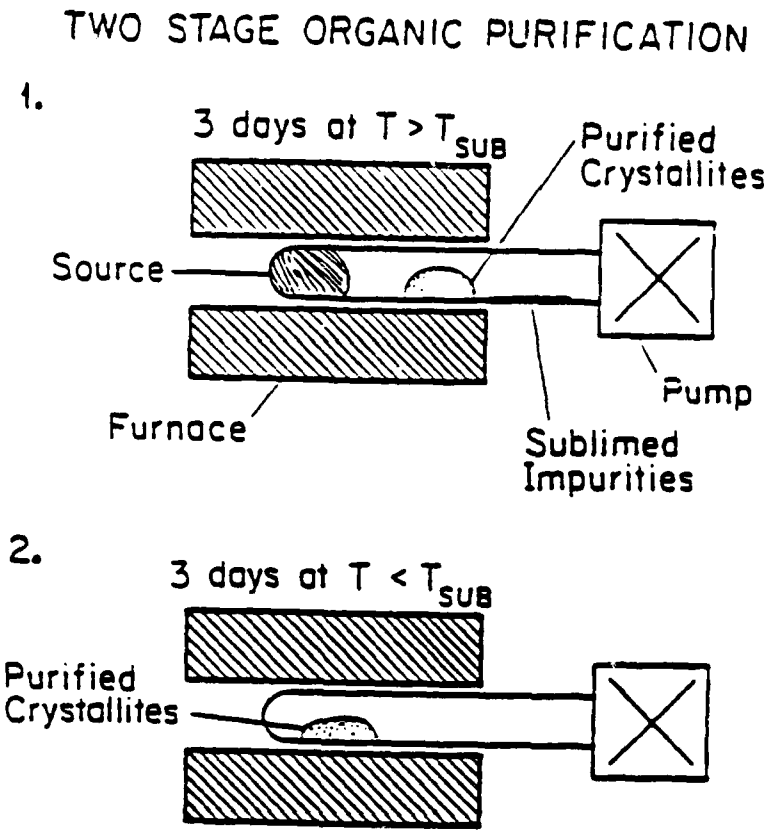


Figure #7 Vacuum sublimation purification for the organic materials.

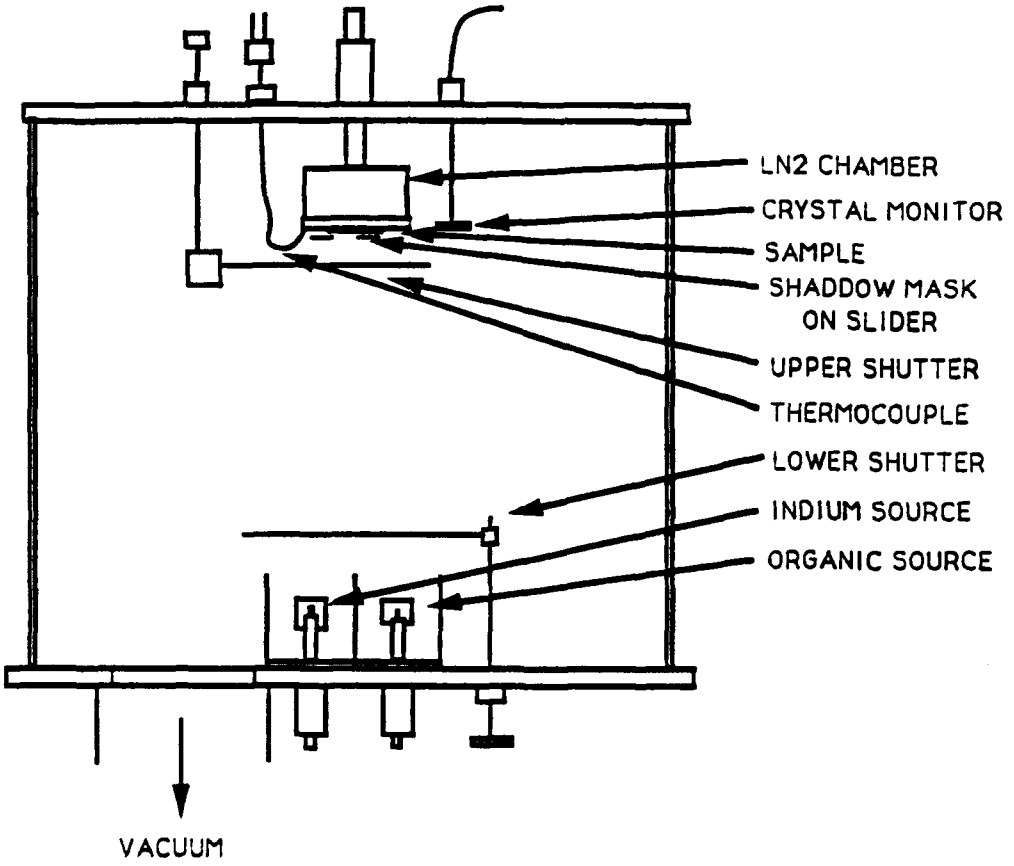


Figure #8 Deposition chamber for the organic and indium metal. The sample is cooled to near liquid nitrogen temperatures. A slider moves a shadow mask over the sample after the organic deposition and before the indium deposition.

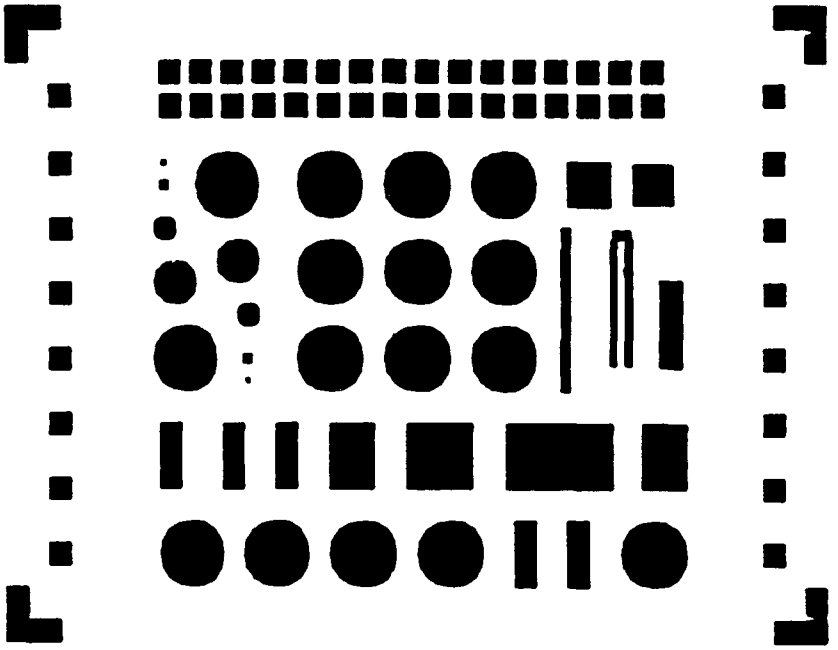


Figure #9 Shadow mask for the metal deposition to define the junction areas for the organic-diodes.

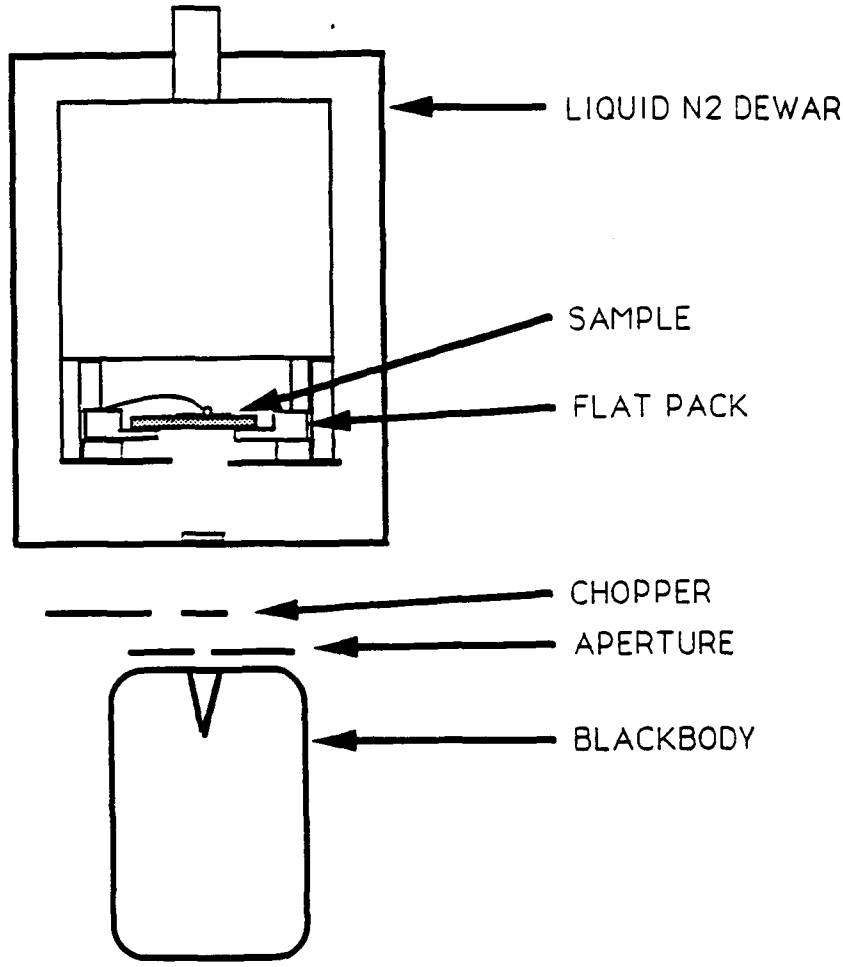


Figure #10 Diagram of the optical test station with calibrated light flux from a blackbody going through a hole in the flatpack to hit the CdT backside of the detector.

RESULTS

Surface Treatment and IV Results

Ten depositions were made using CuPc on HgCdTe and PTCDA on InSb with variations in the surface treatment. Initial screening was done in a nitrogen-atmosphere probe station at room temperature and at liquid nitrogen temperature.

The surface treatments for HgCdTe were:

A) 1% bromine in methanol for one minute,

B) 1% bromine in methanol for one minute followed by H-100 etch for 15 sec.s
(H-100 etch is 70gm KOH, 4gm Tartaric acid, 8gm EDTA, 78 ml DI water mixed 1:1 with 30% hydrogen peroxide),

C) 1% bromine in methanol for 1 min. followed by 10% hydrogen peroxide for 2 mins.

Air exposure in loading the bromine etched samples in the evaporator would leave about 15 Å of native oxide on the surface while the peroxide, C, would leave an oxides of 30 to 50 Å. H-100 etch supposedly leaves a near stoichiometric surface on InS but the H-100 etch is a competition between oxidation and oxide stripping and it can leave a thin surface oxide. The RoA ranges obtained are given in Table 2 and example IV curves are shown in Figures 11 to 14.

The diode results showed much more variability than those seen on wider-bandgap semiconductors such as silicon, GaAs or CdTe. Diode resistance at zero bias times the diode area (RoA) is a common value for evaluating the quality of IR detector diodes. RoA values for the organic on HgCdTe or InSb varied by two orders of magnitude over one square centimeter test wafers.

Many of the IV curves showed a curve shape characteristic of tunneling through an insulating barrier with a high resistance near zero volts and exponentially increasing currents at high plus and minus voltages. The RoA values at room temperature increased drastically with increasing the oxide thicknesses. The current voltage curves are modeled in a following section.

The best RoA values for the thin barrier bromine/methanol etched organic/HgCdTe samples at 77K obtained in this program were about a factor of ten lower than the best values for double-layer or ion-implanted commercial diodes. The room temperature values were several orders of magnitude better than standard diodes.

Table 2: Resistance Area Product at Zero Bias (RoA) at 77K and 300K for HgCdTe and InSb as a Function of Surface Treatment.

Inorganic Semicond.	Type	Carrier Conc. (cm-3)	Organic	Surface Treatment	77K RoA (ohm cm^2)	300K RoA (ohm cm^2)
HgCdTe x=0.23	p		CuPc	Br/Methanol	25-100	6
x=0.25	n	2 e 15	CuPc	Br/Methanol	1 e 3	6
x=0.29	n	2 e 15	CuPc	Br/Methanol	1 e 3 - 1 e 4	50-60
x=0.31	n	2 e 15	CuPc	Br/Methanol	3 e 3	2
x=1.0	p	5 e 14	CuPc	Br/Methanol		1 e 5
x=0.29	n	2 e 15	CuPc	Br/Meth/H-100	1-4 E 4	20, 1e3-1e4
x=0.29	n	2 e 15	CuPc	Br/Meth/H_2O_2	$> 10^8$	1e3,1e7-1e9
InSb	n	4 e 14	PTCDA	Lactic/Nitric	1 e 5	3 e 2
	p	1 e 17	PTCDA	Latic/Nitric	1 e 4	10
	n	4 e 14	PTCDA	L/N/H-100	3e3-1e9	>1e3
	n	4 e 14	PTCDA	L/N/H_2O_2	5e4-2e6	1e3-1e4

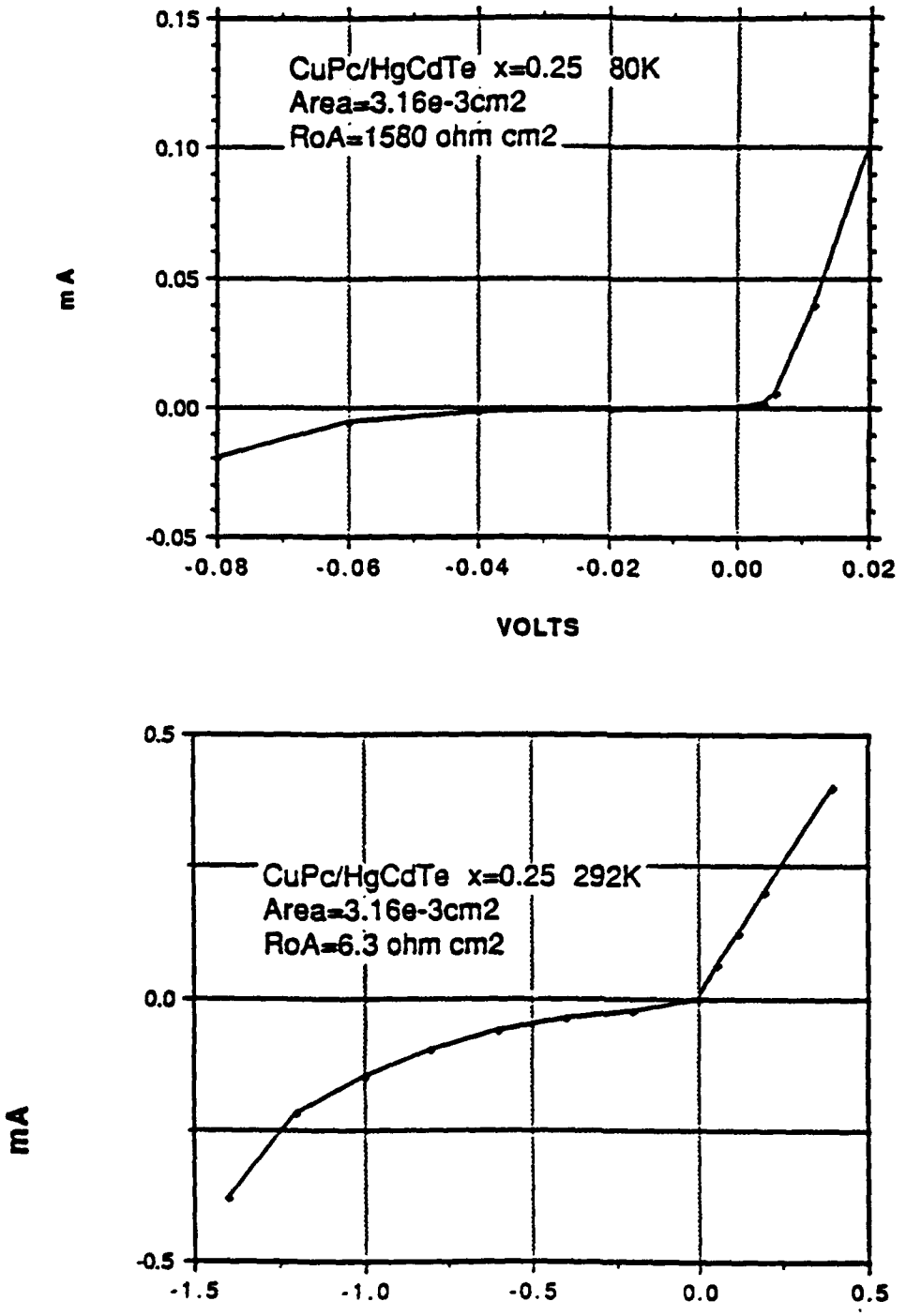
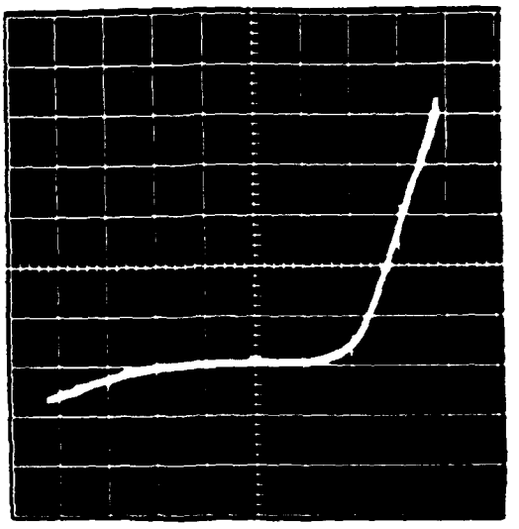
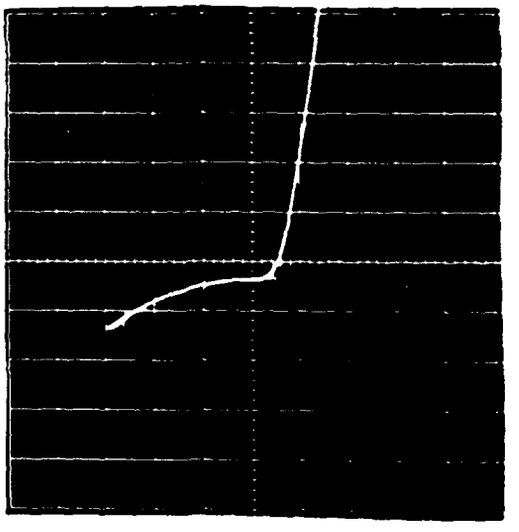


Figure #11 Current-voltage curves at 80K top and 295K bottom for x=0.25 HgCdTe/CuPc sample with Br/ methanol surface treatment.

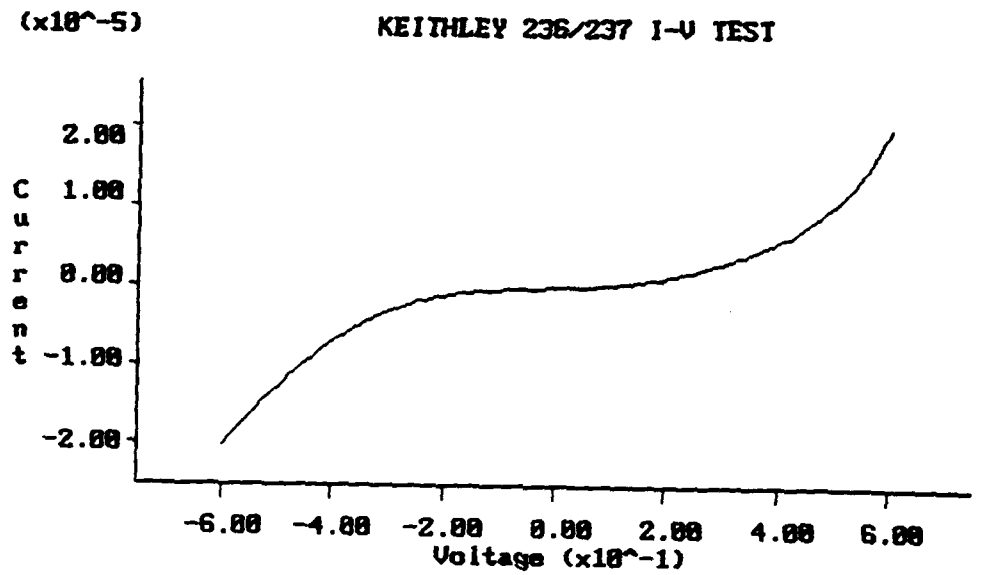


A). scales 0.2V/div. vert., 0.005mA/div. hor.,



B). scales 0.5V/div. vert., 0.02mA/div. hor.

Figure #12 Current-voltage for x=0.29 HgCdTe/ CuPc at 77K with Br/methanol surface treatment. RoA values estimated above 2e4 and 5e3 ohm-cm^2 for top and bottom respectively.



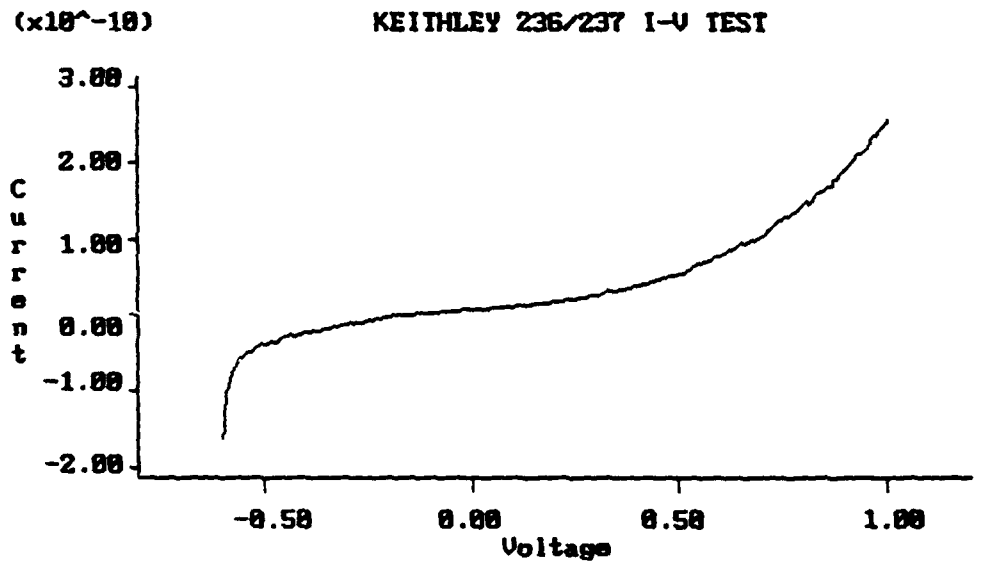


Figure #13 Current-voltage data for x=0.29 HgCdTe/ CuPc at 295K with Br/ methanol/ H-100 etch top and hydrogen peroxide 2 min. bottom. The curves both show surface insulator barrier tunneling characteristics with the RoA values of 1e4 top to 1.5e8 ohm-cm^2 bottom increasing with expected oxide thickness.

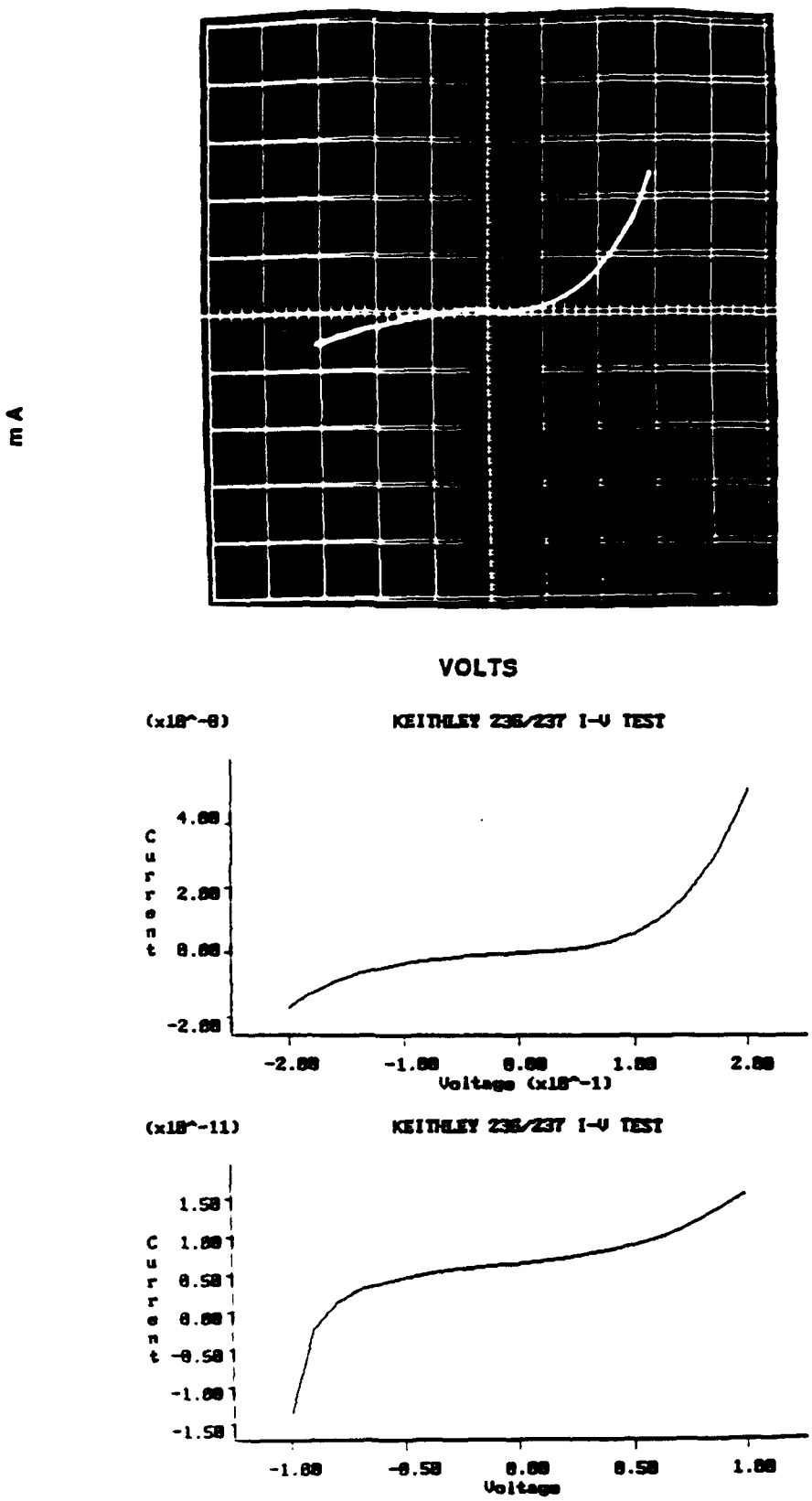


Figure #14 Current-voltage data for InSb at 77K with lactic/nitric surface treatment top, H-100 middle and hydrogen peroxide bottom. RoA values are > 1e4, 1e9 and 1e6 ohm-cm^2 respectively.

Temperature Dependence

RoA data for two bromine/methanol etched samples (process A and B respectively) are shown in Figures 15 and 16 with figure 15 also showing data from a standard double-layer diode(8). The organic diode has poorer RoA values at low temperatures and better RoA values at high temperatures than the standard diode. Modeling in a section to follow suggests the low temperature leakage and RoA is tunneling dominated for the organic. Reducing the tunneling will improve the low temperature RoA values.

IR Detector Quantum Efficiency

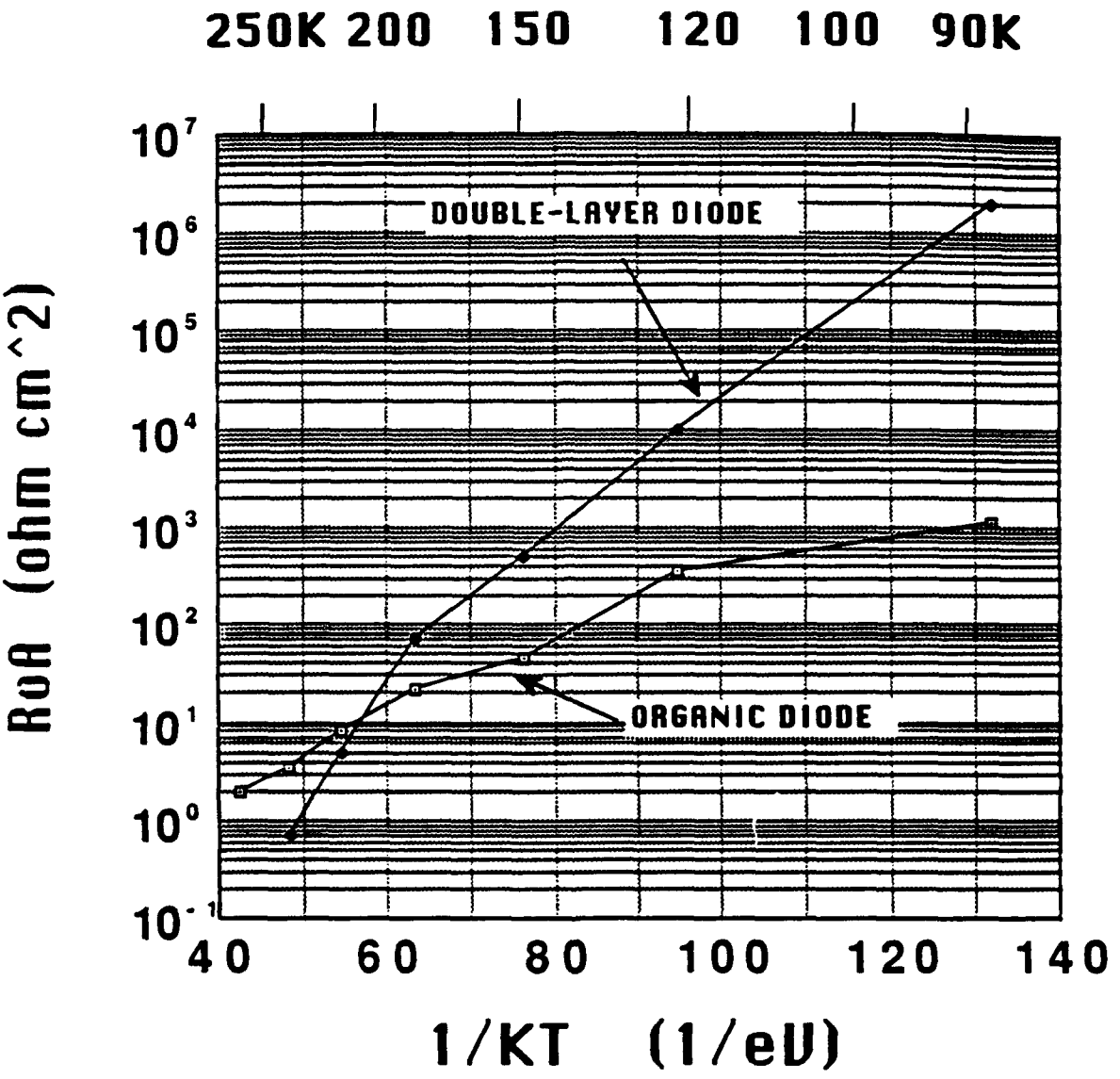
The major issue of this program was to determine whether the organic/HgCdTe or InSb barrier diodes are good IR photo-detectors. Low high-temperature leakage currents and large reverse-bias breakdown voltages have been seen with the organic diodes but was this because there were barriers that would also limit the collection of photo-generated carriers?

Quantum efficiency data was taken on a standard IR test station using a black body at 500 C. The samples were mounted in an 84 pin flat pack with a hole in the bottom , wires were bonded to the indium diode areas using silver filled epoxi, and the flat-pack mounted with the flat-pack hole toward the dewar window. This is diagrammed in Figure 10. Known fluxes of photons from the blackbody go through the hole, through the wide band-gap CdTe substrate backside and into the HgCdTe epitaxial layer where they generate minority carriers. There is a 23% loss of photons due to the surface reflections plus losses expected from surface roughness and crystal defects.

Figure 17 shows the IV curve for x=0.29, n-type (2e15), HgCdTe at 80K with two photon fluxes. The surface treatment for this sample was 1% bromine/methanol for one minute then H-100 etch for 15 seconds. The quantum efficiency is 0.62 using the diode junction area. This value is close to what is expected with losses due to the CdTe surface reflection and scattering. It is similar to values seen in non-AR coated standard diodes (ion-implanted or double-layer). Quantum efficiency as a function of temperature is shown in Figure 18. There is no slope to the data. No thermal barrier to minority carrier collection is seen.

Figure 19 shows data from another diode (#14) from the same test sample. This diode does show characteristics of a minority carrier barrier. This is seen in the drop in photo current near zero bias. The quantum efficiency near zero bias in this diode is only a few percent. A bias of ~0.025 volts provides enough field to allow the optically generated carriers to tunnel through the barrier.

The data shows that organic/ HgCdTe diodes can be made that have high quantum efficiencies and no barriers that perform as good IR detectors, but that barriers can also occur and they will degrade photo collection.



Figure#15. RoA verses temperature for an organic diode (CuPc/x=0.31 HgCdTe, Br/methanol surface) and a double-layer epitaxial diode (x=0.29 HgCdTe).

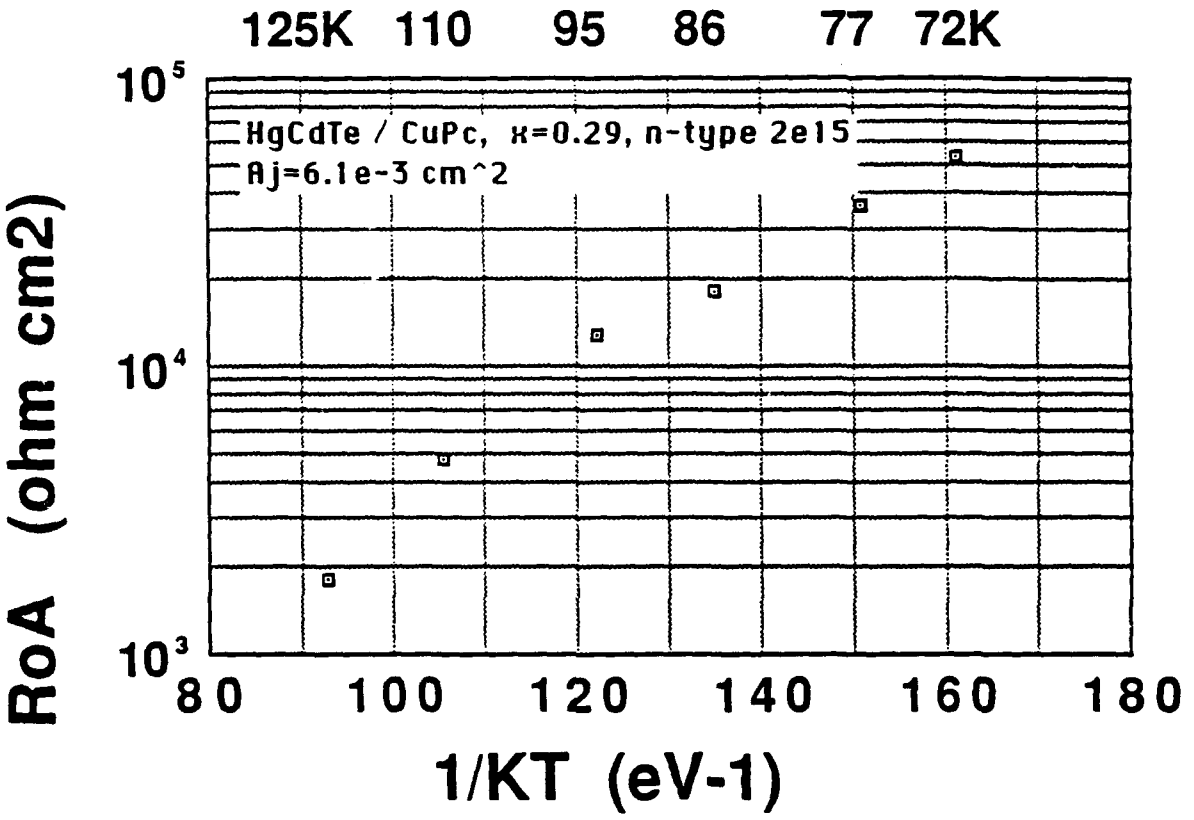


Figure #16 Zero bias resistance area product vs. temperature for CuPc/ x=0.29 HgCdTe. Surface H-100.

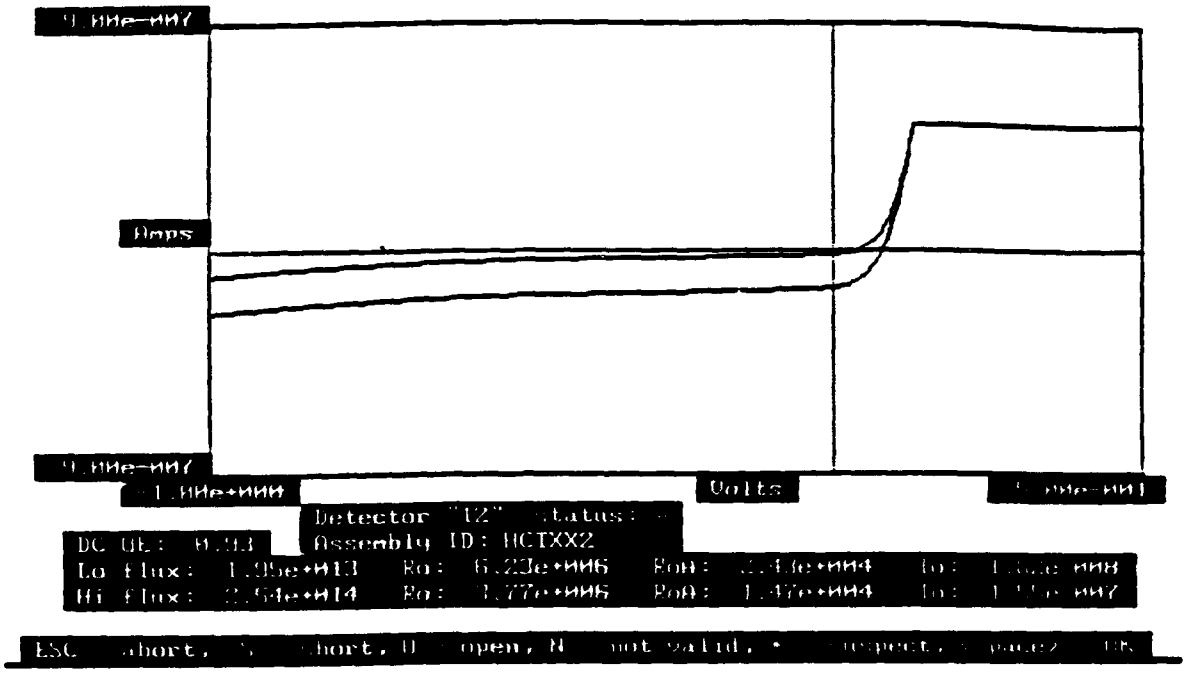


Figure #17 Current-voltage for Diode #12 x=0.29 HgCdTe/CuPc, H-100 etch, at fluxes of 1.95 e13 and 2.54 x e14 photons/cm^2 sec. The quantum efficiency is 0.63 using the junction area of 6e-3 cm^2.

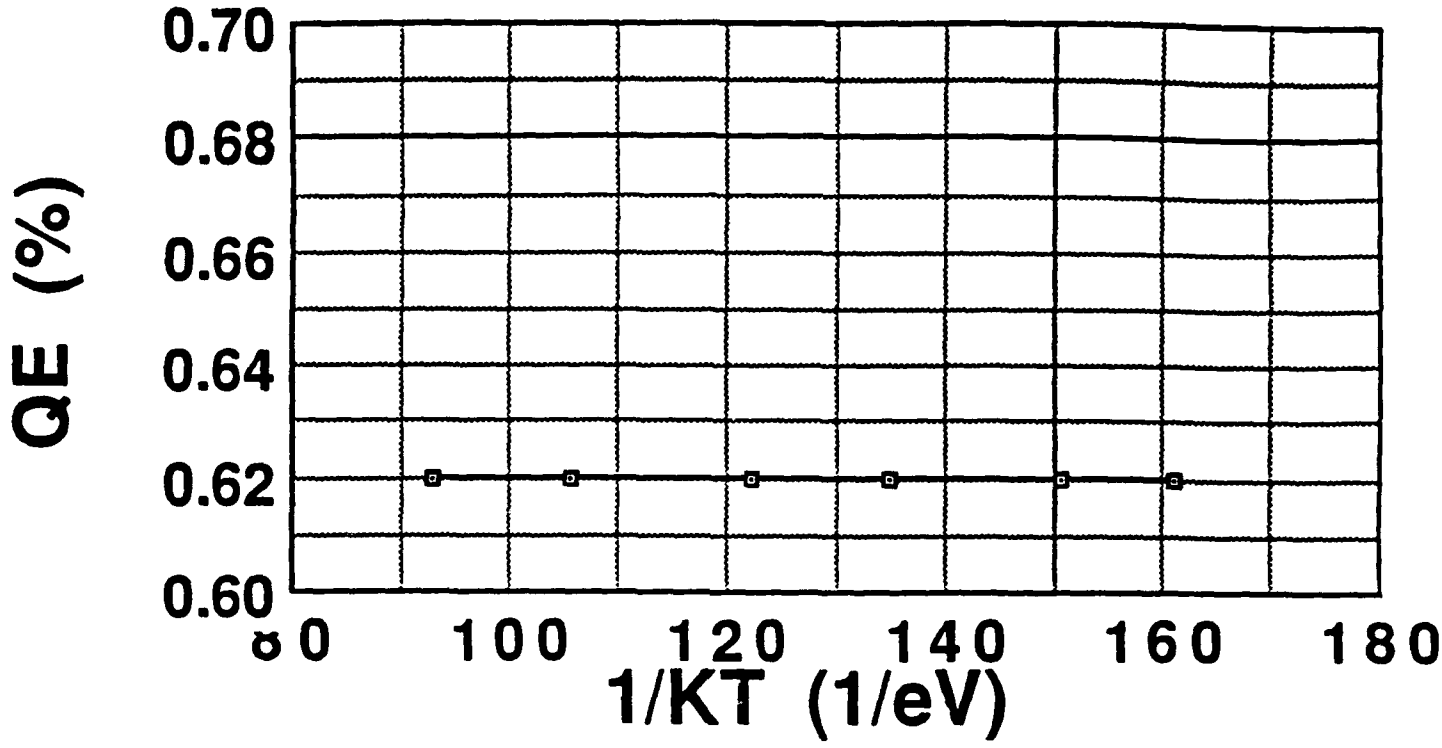


Figure #18 Quantum efficiency as a function of temperature for diode #12 CuPc on x=0.29 HgCdTe.

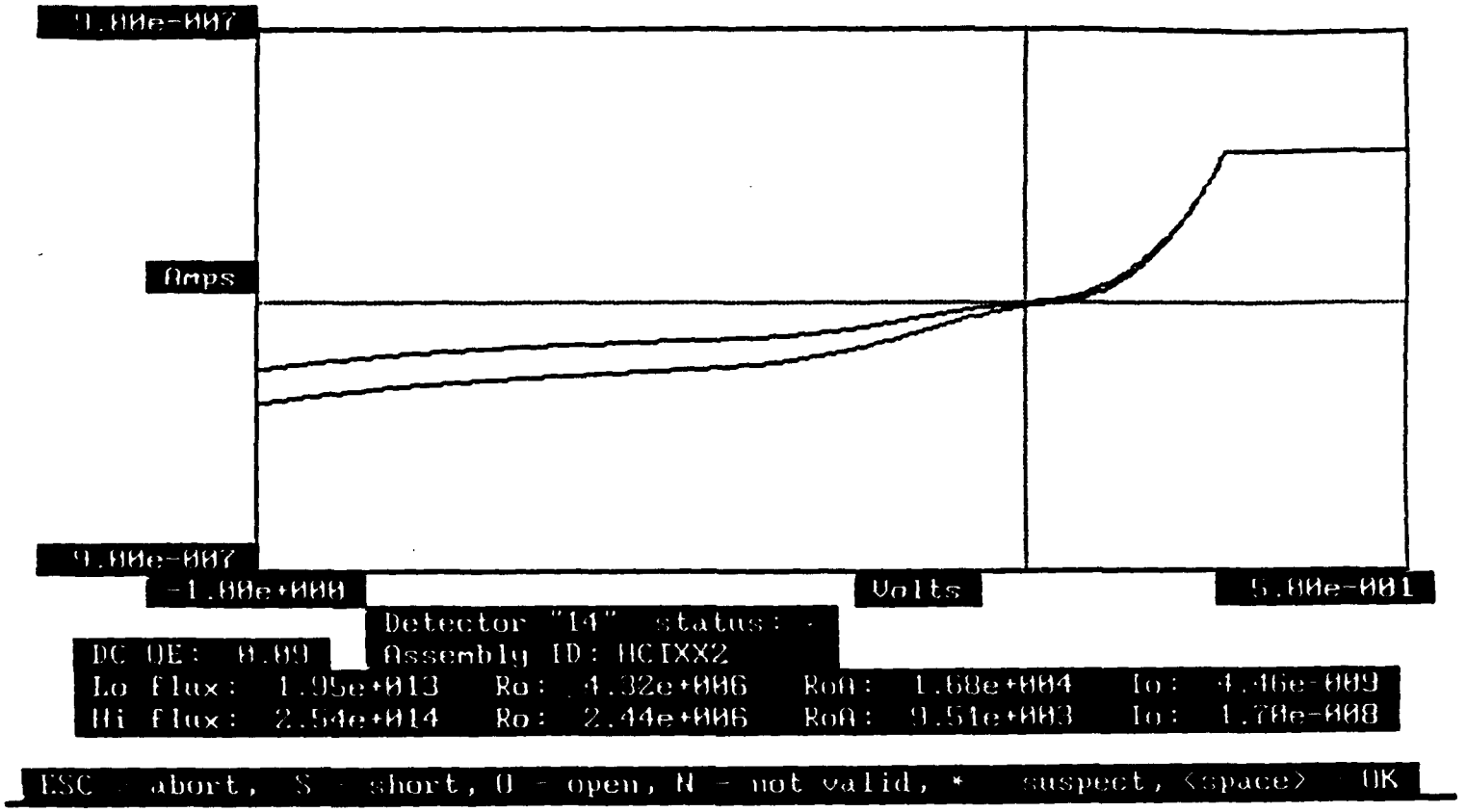


Figure #19 Current-voltage data for Diode #14 at 77K showing a drop in quantum efficiency near zero bias.

1/f Noise

1/f noise was measured for the same samples used for the quantum efficiency measurements above. Data for the diode that did not show a barrier (#12) is shown in Figure 20. Excess noise is seen that increases as 1/f and as the reverse bias is increased. The 1/f noise in this diode is larger than that reported for double-layer x=0.3 HgCdTe (9). The 1/f noise in this organic diode increases much faster with voltage than the depletion region generation-recombination current or diffusion current. The 1/f noise seems to follow the tunneling current component that can be seen at high voltage and is the cause of the reverse breakdown.

Tunneling, if it occurs, is a strong source of 1/f noise(9). It was hoped that the organic/semiconductor diodes would have lower 1/f noise than standard junction diodes because they have less pinch-off field at the diode surface. This would lower the surface tunneling. The tunneling seen in diode #12 may be due to band bending at the junction.

Diode #14 showed a barrier to minority carrier collection and higher tunneling leakage current in reverse bias than diode #12. The noise at 0.025 V reverse bias is compared for these two diodes in Figure 21. The 1/f noise is much higher in diode #14 with the barrier and the higher tunneling leakage.

At this point we are comparing the 1/f noise from some of the first organic/HgCdTe diodes with data from some of the better commercial diodes that have had over fifteen years of process development. The current data showing higher 1/f noise data for the organic diodes may not hold up after further development. Another result is that while the diode IV curves and RoA data may look better for junctions with insulating layer barriers, both the quantum efficiency and the 1/f noise are better for surfaces with no added barriers.

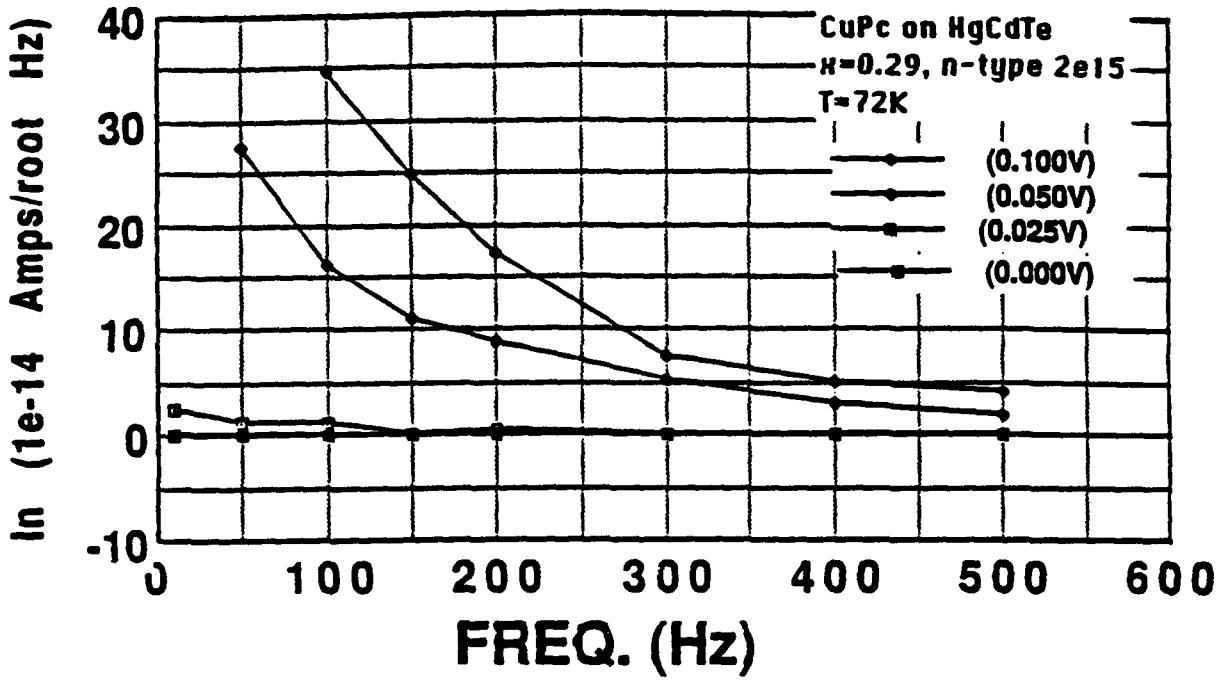


Figure #20 Excess noise as a function of frequency and reverse bias for Diode #12 x=0.29 HgCdTe/CuPc.

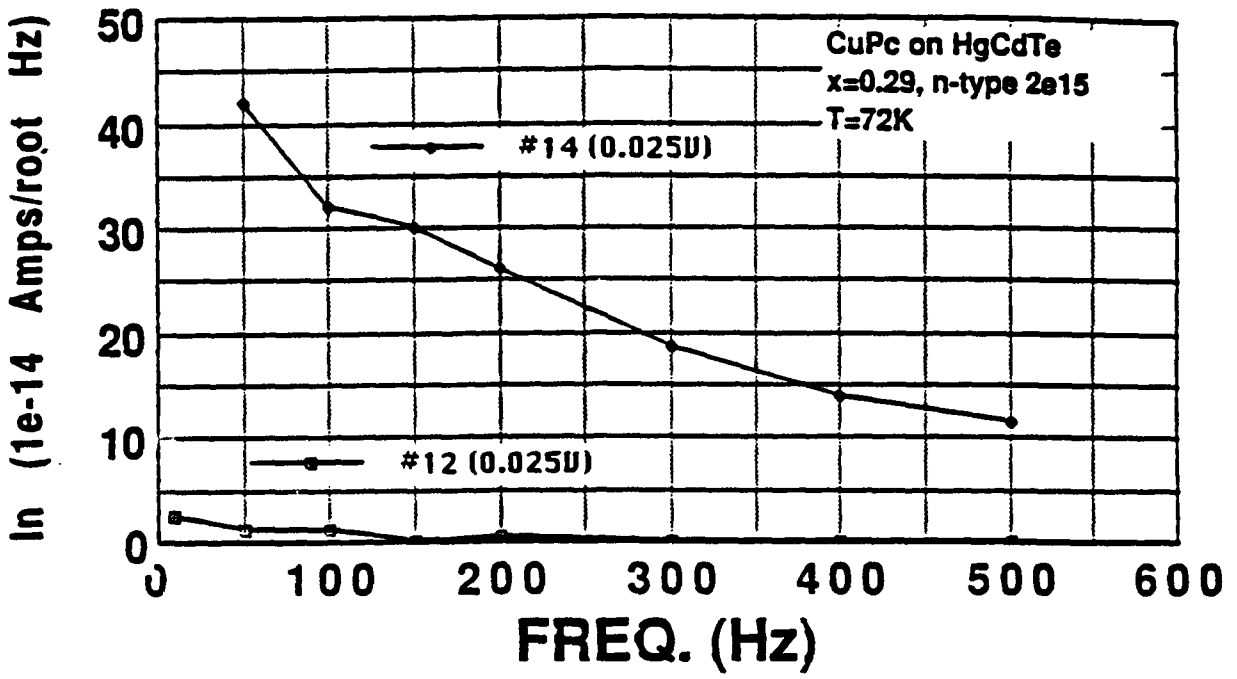


Figure #21 Noise comparison for Diode #12 and #14 at -0.25V reverse bias.

IV Modeling

Early analysis of the organic/inorganic heterojunction devices treated them as a metal-semiconductor Schottky diode (10). The current density is given by:

$$J = Jos\{exp(qVd/KT)-1\} \qquad 1$$

with the saturation current given by

$$Jos = A^*T^2exp(-q\phi b/KT) \qquad 2$$

where Vd is the inorganic voltage drop, A* is the Richardson constant, and øb is the apparent energy barrier. A model that includes both the ohmic conduction of the organic films at low fields and the space charge limited conduction at high fields along with diffusion and drift currents is given in Frankie So's thesis (2). The carrier velocities change as the field goes from low field resistive conduction in the organic to high fields where the organic is space-charge limited. In this model the saturation current is given by

$$Jos = qNs\{vc\}exp(-\phi bp/KT)/(1+\{vc\}/vd) \qquad 3$$

where Ns is the inorganic majority carrier band effective density of states, {vc} is the average carrier velocity in the organic film, vd is the inorganic diffusion velocity and øbd is the barrier diffusion potential. A plot of the log of the saturation current as a function of 1/T was made for the x=0.31 HgCdTe sample at -0.05 and -0.30 volts reverse bias.

The data are shown in Figure 22 and the slope gives a barrier energy for the x=0.31 n-type HgCdTe/ CuPc heterojunction of 0.16 ±0.02 eV. Analysis of the Schottkey model, equation 4, using a Richardson constant proportional to the electron effective mass (A*= 120 x 0.014= 1.68K^-2cm^-2) gave a similar barrier value of 0.19 ±0.04 eV.

The model above works well for the wider band-gap semiconductors but for HgCdTe and InSb tunneling is also important. In the low voltage linear region the forward bias the current density is

$$J \sim exp(-Eg/nKT) \qquad 4$$

At temperatures below 88K n=3.5 indicating that tunneling dominates the current flow while at higher temperatures n=2 and the depletion region generation-recombination current dominates. For many of the organic/HgCdTe or InSb diodes especially the samples with thick oxides, the current looks like MIS tunnel currents(11) where

$$J \sim V^2 exp(-b/V) \; . \qquad 5$$

Current vs. Temperature

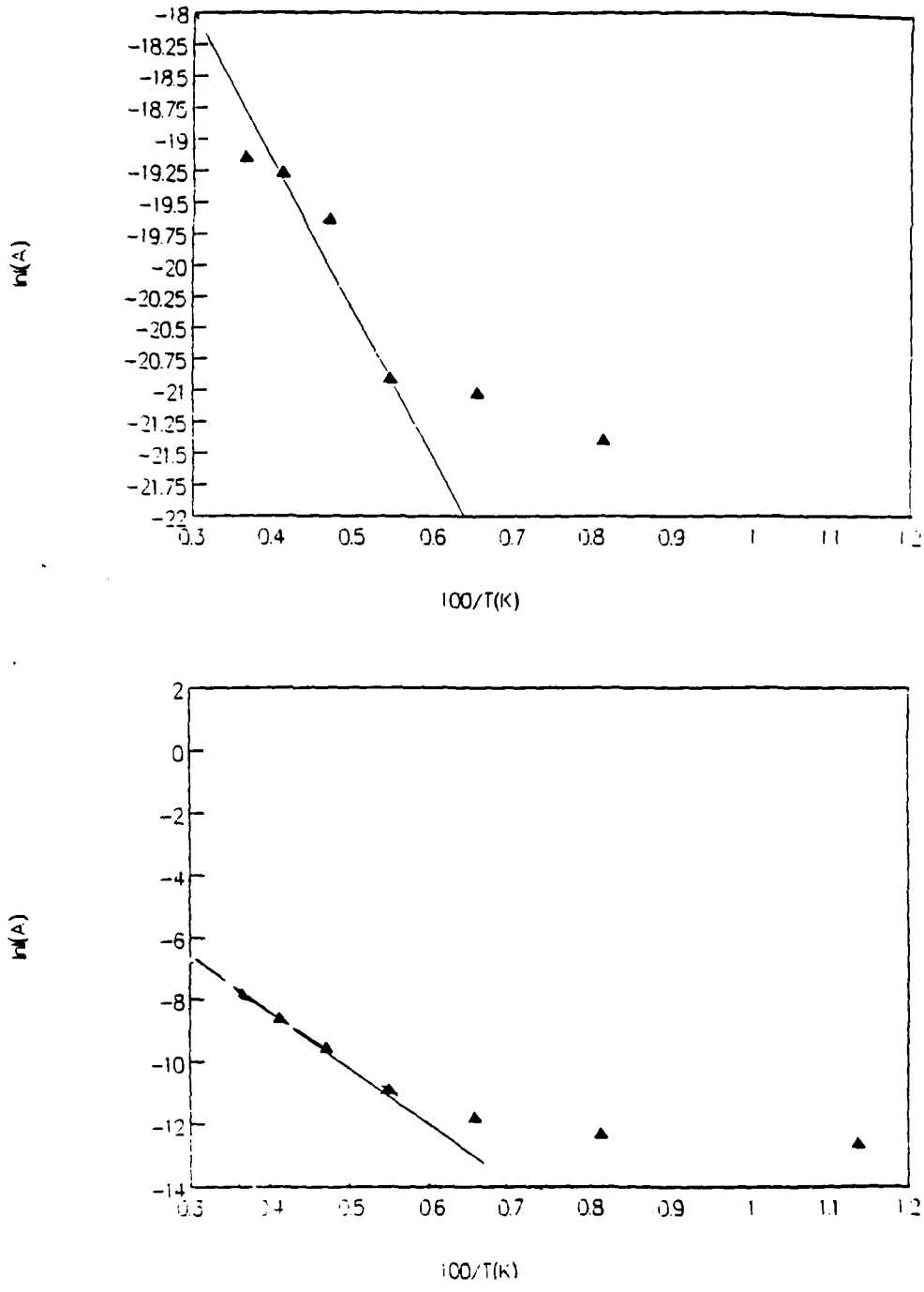


Figure #22 Log current vs. 100/T for the x=0.31 HgCdTe/ CuPc (Br/ methanol surface) at -0.05 V top, and -0.3 V reverse bias bottom. The activation energy at both biases from the slope is 0.16 ±0.02 eV.

At low biases the resistance is high but at high voltages tunneling current exponentially increases with bias. This type of IV curve is seen in the oxidized sample shown in Figure 13.

PROCESSING

The organic materials are very soft and are water sensitive making handling and storing the devices difficult. Several processing changes were tried to see if techniques more usable for IR array production could be found.

Because the organics absorb water which degrades the electrical properties, the purified organics and the test wafers were stored in dry boxes. The probe station was purged with dry nitrogen gas so that water would not condense on the samples as they warmed from nitrogen temperature.

In order to protect the samples from water vapor, low temperature silicon nitride was used as a cap material over the organic and metal layers. Silicon nitride deposited at 100 C in a plasma electron cyclotron resonance CVD system was able to cap the devices and have holes opened in the nitride using HF etch over the metal contacts without degrading the diodes. See the bottom of Figure 2 for a diagram.

Even with the silicon nitride cap, problems occurred in temperature cycling the test samples. Rapid cooling and warming in the probe station made the organic layer blister and separate from the HgCdTe. The same samples cycled without any separation in the test dewar which takes about a half an hour to cool and several hours to warm up.

An attempt was made to see if the diodes could be hybridized to a fanout which is a step in the current two dimensional IR array processing. Thick indium (4 microns) was used as a metal contact on the organic. A fanout with indium bumps on it corresponding to each of the test diodes was pressed against the test wafer but the organic did not have enough strength to hold the fanout and it pulled free of the HgCdTe.

Another process was tried in which the silicon nitride was deposited on the HgCdTe and holes opened in the nitride at the diode areas. The organic and the contact metal were then deposited over this. This gave a structure with the organic in contact with the HgCdTe in the diode areas and a metal layer over the organic. It was hoped that the metal layer would protect the organic and the regular photolithography could be used to define the metal areas. Undercutting and metal porosity were enough so that exposure to photoresist, photoresist developer or acid metal etches disolved the organic.

At this point processing is adequate for test device processing but not for array manufacturing and more work in process development is needed.

MATERIAL CHARACTERIZATION

One of the uses for the organic/semiconductor devices has been the non-destructive characterization of semiconductor material (12). PTCDA washes off with basic water without damaging the semiconductor. The long times and high pH needed to remove CuPc from HgCdTe was found, however, to damage the HgCdTe surface. The CuPc could also be removed in acid solutions and with organic solvents. At present the organic removal from HgCdTe is not as nondestructive as with the other semiconductors as destinct patterns were left in the HgCdTe surface of the diode regions where the metal contact protected the material under it to some extent before the metal came off.

In this program the capacitance in reverse bias was measured for a diode formed with CuPc on x=0.31 HgCdTe. The data is shown in Figure 23. Using the abrupt junction model, the carrier concentration was calculated as a function of depth in the HgCdTe using (9):

$$1/C^2 = 2(Vbi-V-KT/q)/(q\ es\ Nd) \qquad 6$$

$$Nd = 2/(q\ es)\{-1/d(1/C^2)/dV\} \qquad 7$$

where Vbi is the built in voltage of the junction, V the applied voltage, and Nd is the donor concentration and es is the static dielelectric constant. The built in voltage was found from the $1/C^2$ verses V curves with the linear region extrapolated to V=0. The built in voltage was 0.3 V. The doping density as a function of depth into the HgCdTe is shown in Figure 23.

The organic diodes have demonstrated the ability to do characterization of carrier profiles. Other characterizations that also depend on reverse bias testing such as DLTS impurity testing should also be possible. At present the RoA values are too scattered and too dependent on surface barriers that vary to be used to test leakage or RoA uniformity.

C-V Measurement

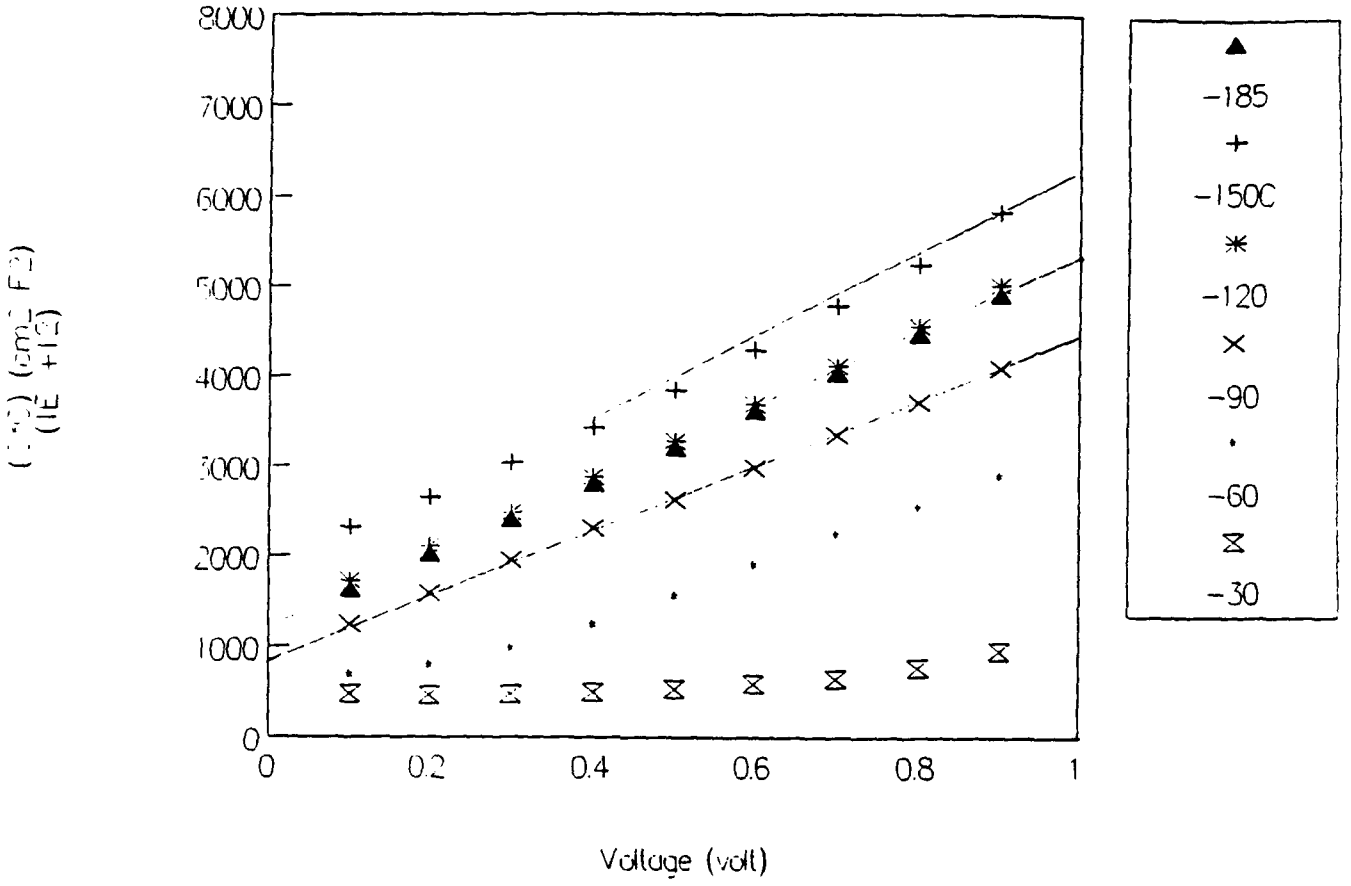


Figure #23 The capacitance vs voltage for the x=0.31 HgCdTe/CuPc diode plotted as 1/C^2. The zero voltage extrapolations gave a built in voltage of 0.3 volts for the organic/ x=0.31 HgCdTe heterojunction.

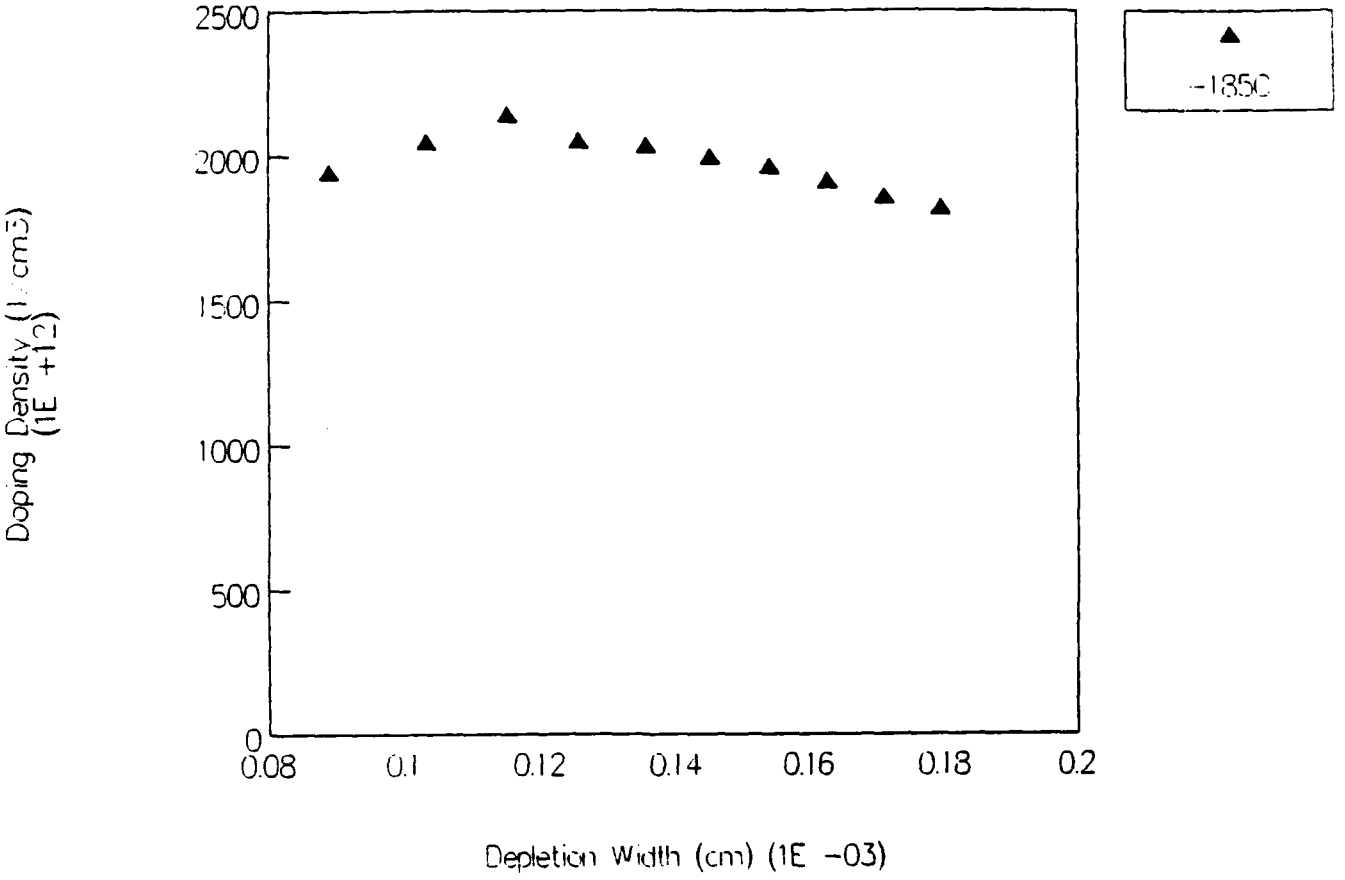


Figure #24 The doping profile for the x=0.31 HgCdTe at 88K as determined from the reverse-bias capacitance vs voltage data.

PROGRAM OBJECTIVE RESULTS

This program was able to meet almost all of the Phase 1 objectives. The specific objectives were the following:

- Evaluate two organic materials with good junction properties on HgCdTe.

CuPc was evaluated on HgCdTe and shown to give good electrical and optical data. A second organic did not make it through purification in time to be used in this program. PTCDA produces poor diodes on HgCdTe but reasonable diodes on InSb.

- Charactize the optical detector properties.

Good IR detectors were demonstrated with CuPc on HgCdTe with quantum efficiencies comparable to standard ion-implanted or double-layer detectors. Diodes were made with no temperature dependence to the quantum efficiency and no sign of thermal barriers. The RoA values were higher than standard diodes at room temperature and lower than standard diodes at liquid nitrogen temperature. Initial detector 1/f noise for the organics was larger than that in standard HgCdTe diodes and seemed to follow the tunneling current component of the leakage current. If the tunneling current can be reduced in future devices, the low temperature RoA will increase and the 1/f noise will be reduced. Diodes with barriers were seen that degraded the quantum efficiency and increased the 1/f noise. It is possible to make diodes with insulating layers at the junction. These have very low leakage currents and very large reverse bias voltages. They can be operated in reverse bias to obtain reasonable quantum efficiencies but the 1/f noise would be very large.

- Evaluate the DoD and commercial potential of these devices.

The major benefits of the organic heterojunction process have been sustantiated. Detectors have been demonstrated with the same quantum efficiencies as regular detectors and with lower high-temperature leakage currents than regular detectors. These have been made with a junction formation process that is low-temperature, non-damaging to the original material, simple and low cost.

There is commercial potential for these devices but the realization of this potential depends on the further optimization of the processing. At present the processing can produce test devices and small arrays but the yield and uniformity are too low for commercial production. The high-temperature operation requires the identification of low-resistivity, ohmic metal contacts. Large two dimentional arrays require the developing of new processing procedures. Modeling including tunneling would be very helpful for these small bandgap materials. A Phase 2 or joint university/ industry program is the next step needed.

CONCLUSIONS

The major conclusions of this phase 1 program are:

- High quantum efficiency IR diodes can be made using evaporated organics,
- The high temperature RoA values are better than those seen in commercial diodes,
- Higher temperature detector operation should be possible with these devices,
- The organic devices can be used for reverse bias materials characterization in the narrow-bandgap materials,
- The process is very simple and low cost, but the current yields are low and the process needs more development for array production,
- Current 1/f noise is dominated by tunneling and is higher than in commercial diodes, and
- Optimizing the organic diodes for low leakage is not enough for IR detectors since barriers can lower leakage but degrade quantum efficiency and 1/f noise.

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